# S P E C I F I C A T I O N

# TO ALL WHOM IT MAY CONCERN:

Be it known that Richard L. Antrim, citizen of the United States, and resident of Solon, Iowa, has invented certain new and useful REDUCED MALTO-OLIGOSACCHARIDES of which the following is a specification.

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## REDUCED MALTO-OLIGOSACCHARIDES

# RELATED APPLICATION

The present application claims priority to prior U.S. Patent Serial No. 09/366,065, filed August 2, 1999, which application continuation of International was а Application PCT/US99/01098, filed January 19, 1999, which application claimed priority to prior United States Provisional Application Serial No. 60/071,905, January 20, 1998. The entire contents of each prior application are hereby incorporated by reference.

### TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to reduced malto-oligosaccharide species and methods for the preparation thereof.

# BACKGROUND OF THE INVENTION

Oligosaccharides are commonly prepared the controlled hydrolytic cleavage of starches. the production of such oligosaccharides, the glycosidic linkages of the starch molecules are partially hydrolyzed to yield at least one oligosaccharide species, and more typically, a mixture of oligosaccharide species. oligosaccharide species in the mixture characterized by its degree of polymerization (DP), which refers to the number of saccharide monomer units in the molecule. Each oligosaccharide species also may characterized by its dextrose equivalent (DE), generally indicates the proportion of aldehyde, hemiacetal

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or ketone terminal groups in the molecule, and which is a of the reducing sugar content of the measure oligosaccharide, expressed as a percentage of the total dry substance. The DE value and DP profile for a given oligosaccharide mixture can vary substantially, depending, for example, upon the type of starch precursor used to obtain the mixture and the conditions employed for hydrolysis of the base starch.

Oligosaccharide mixtures prepared by the hydrolytic cleavage of starch typically include at least one malto-Malto-oligosaccharides oligosaccharide species. characterized backbone as having a saccharide that comprises predominantly 1-4 glycoside linkages. oligosaccharides having a DE less than 20 are known as maltodextrins, whereas malto-oligosaccharides having a DE of 20 or greater are known as syrup solids.

is in the art to reduce malto-Ιt known oligosaccharides and other starch hydrolyzates by reducing the terminal groups in the malto-oligosaccharide or starch hydrolyzate molecule. Such reduced malto-oligosaccharides and other starch hydrolyzates are useful in a variety of applications, including, for example, sweetening agents and texturing agents in products intended for ingestion by Examples of such products include animals or humans. sweets, chewing gums, syrups, food additives. pharmaceutical agents, and so forth. Typically, starch hydrolyzates have been reduced via enzymatic, catalytic, or chemical methods. For example, U.S. Patent 2,280,975 describes a process for the production of polyhydric alcohols via catalytic reduction of monoand

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disaccharides. A more recent patent, U.S. Patent 4,322,569, discloses the reduction of monosaccharides by contacting the monosaccharide with hydrogen in the presence of a nickel catalyst in a catalytic bed.

Known processes for the reduction of and starch hydrolyzates suffer from a number of drawbacks. For example, it is often desired to reduce maltooligosaccharide to a DE of zero or essentially zero. Typically, such would be accomplished by substantially catalytically hydrogenating completely the maltooligosaccharide until the desired DE value is obtained. When malto-oligosaccharides are reduced in accordance with such methods, however, the polysaccharide backbones of the individual species in the mixture may become cleaved, as reported, for example in the aforementioned U.S. Patent 2,280,975 with regard to the reduction reaction disclosed Such cleavage of the polysaccharide backbone will cause the DP of the cleaved species in the maltooligosaccharide to become lower, and will cause alteration in the overall DP profile of the oligosaccharide mixture. Such alteration of DP profile may cause certain physical properties of the mixture, such viscosity, to change, thus potentially requiring alteration of processes in which the mixture is intended for use.

Another problem in the art pertains to the color-fastness of malto-oligosaccharides. Malto-oligosaccharides are typically characterized by having a non-zero DE value. One problem with known malto-oligosaccharides is that solutions thereof may tend to

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yellow under certain conditions, for example, conditions of heat, alkaline pH, or traces of nitrogencontaining compounds, thus causing visual degradation of the product in which the malto-oligosaccharide incorporated or other undesired effects. This tendency towards color formations is indicative of the chemical reactivity of the malto-oligosaccharides under foregoing conditions, particularly towards compounds.

In light of these shortcomings in the art, there exists a need for a method for reducing a maltooligosaccharide to a DE of essentially zero without substantially the DΡ of the altering maltooligosaccharide, and particularly for reducing a mixture of malto-oligosaccharides to a DE of essentially zero without altering substantially the DP profile of the A further need in the art exists for a maltooligosaccharide product having an improved resistance to color formation. The general objects of the present invention are to provide a method and a product that overcome the foregoing drawbacks of the prior art.

# THE INVENTION

The foregoing general objects have been achieved by
the present invention, which provides a method for the
catalytic reduction of an oligosaccharide, and which
further provides a reduced oligosaccharide prepared
thereby. In accordance with the invention, a method for
substantially reducing a mixture of a plurality of
oligosaccharide species is provided. The oligosaccharide

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species may differ at least in DP value, thus defining a DP profile for the mixture. In the preferred embodiment the invention, the method comprises the steps of providing the oligosaccharide mixture, and catalytically hydrogenating the mixture under hydrogenation conditions suitable to substantially preserve the DP profile of the Surprisingly, it has been found that catalytic mixture. hydrogenation of oligosaccharides such as maltodextrins in the presence of a metal catalyst, such as platinum, palladium, ruthenium, rhodium, or nickel, at temperatures ranging from about 50° C to about 150° C and pressures of at least about 1500 psi will be effective in substantially reducing the DE of the mixture to zero or essentially zero, without substantially altering the DP profile of the mixture. In another embodiment of the invention, method comprises catalytically reducing an oligosaccharide or mixture of oligosaccharides at a pH ranging from about 3.5 to about 8.5. In either embodiment, the invention is more generally contemplated to be useful in connection with the catalytic reduction of polysaccharides.

In accordance with a preferred embodiment of the invention, a mixture of reduced malto-oligosaccharide species is catalytically reduced. The species differ in at least DP value thus defining a DP profile for the mixture. Surprisingly, it has been found that, when a starting malto-oligosaccharide mixture is catalytically hydrogenated in accordance with the invention, the reduced malto-oligosaccharide mixture thus formed will have a DP profile that is not substantially altered as compared with the DP profile of the starting malto-oligosaccharide

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mixture. It has further surprisingly been found that the resistance to color formation of the reduced malto-oligosaccharide, as measured by the light absorbance thereof, is improved relative to the starting mixture of unreduced malto-oligosaccharides. A liquid mixture of the reduced malto-oligosaccharides will be stable, and, it is believed, relatively more stable than a liquid mixture of unreduced malto-oligosaccharides.

Further features and objects of the invention will be apparent from the following description and appended claims.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the invention is applicable to oligosaccharide species or mixture of a plurality oligosaccharide species, and more generally to polysaccharide species and mixtures thereof. Ву "polysaccharide" and "oligosaccharide" is are contemplated any species comprised of plural saccharide units, whether linked by 1-4 linkages, 1-6 linkages, or otherwise. For example, the invention is applicable in reduction of malto-oligosaccharides and mixtures thereof, as well as other oligosaccharides. By "maltooligosaccharides" is contemplated any species comprising two or more saccharide units linked predominately via 1-4 linkages, and including maltodextrins and syrup solids. In preferred embodiments, in the reduced oligosaccharides of the invention, at least 50 percent of the saccharide units in the malto-oligosaccharide are linked via 1-4 linkages. More preferably, at least about

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60 percent of the saccharide units are linked via 1-4 linkages; even more preferably, at least about 80 percent of the saccharide units are so linked. The malto-oligosaccharides may include saccharide species having an odd DP value, and the profile may be partially defined by a saccharide species having a DP value of 1, for example, dextrose or sorbitol. The mixture further may include other saccharide species or other components.

While the invention finds applicability with respect to any malto-oligosaccharide mixture, the invention is particularly applicable to malto-oligosaccharide species in which at least a portion of the malto-oligosaccharides the mixture have а DP value greater than Preferably, at least one of the malto-oligosaccharide species in the mixture has a DP value of 8 or more. preferably, at least one species has a DP value of at For example, in preferred embodiments of the least 10. 80 the invention, at least percent of maltooligosaccharide species in the mixture have a DP greater than 5, and at least 60 percent may have a DP greater In another embodiment, at least 80 percent of than 8. the malto-oligosaccharides species have a DP greater than In some embodiments of the invention, the DP profile of the starting mixture is such that at least 75 percent of the malto-oligosaccharides species in the mixture have a DP greater than 5 and at least 40 percent of the species in the mixture have a DP greater than 10. Such starting materials may be obtained conventionally, example, by the partial hydrolysis of starch.

Suitable malto-oligosaccharides sold are maltodextrins under the trademark MALTRIN® by Grain Processing Corporation of Muscatine, Iowa. The MALTRIN® maltodextrins are malto-oligosaccharide products, product having a known typical DP profile. Suitable MALTRIN® maltodextrins that may be reduced in accordance invention with the present include, for example, MALTRIN® M040, MALTRIN® M050, MALTRIN® M100, MALTRIN® M150, and MALTRIN® M180. Typical approximate DP profiles of the subject MALTRIN® maltodextrins are set forth in the following table (the DP profiles being approximate as indicated in the table):

			$\Gamma_{\lambda}$	Typical DP	profile	(% dry solids	lids basis)	(3)			
DP profile	M180	80	M	M150	M100	00	M050	0 0 0 0 0 0		M040	~
DP>8	46.6	+ <del>4</del> 4%	54.7	+  %	67.8	+  %	90.6	+4%	88.5	+I %	
DP 8	3.9	+  -  -  -	4.8	+1.5%	4.5	+  -1  -5%	1.5	+  ~~	2.0		
DP 7	9.5	+  -  -	9.1	+1.5%	7.0	+  -  -  -  -	1.5	+  	2.4	+l +l	
DP 6	11.4	+2%	8.4	+1.5%	6.1	+  -1  -5%	1.4	+   -	1.8	+  -	_
DP 5	5.9	+ 2%	4.7	+1.5%	3.3	+  -  -  -  -  -	1.3	*\ 	1.3	+  -  -	
DP 4	6.4	+ 5%	5.5	+1.5%	3.7	+1.5%	1.1	+   -  -  -	1.4	+  -  -	
DP 3	8.3	+2%	6.7	<u>+</u> 1.5%	4.2	+1.5%	1.0	+1%	1.4		
DP 2	6.2	+ 2%	4.8	+  %  -	2.5	+  -  %	*8.0	+   -  -	*6.0	% ⊢ ⊢	
DP 1	1.8	<u>+</u> 1.5%	1.3	+1%	*4.0	+  ~ ~	*8.0	+   -  -  -	0.3*	+I ~L	
* MINIMUM VALUE	п	%0									٦.

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The invention encompasses reduced maltodextrins having substantially the foregoing approximate DP profiles, however made. Other suitable malto-oligosaccharides such MALTRIN® include other maltodextrins, as MALTRIN® 4510, MALTRIN® M550; MALTRIN® M580, an MALTRIN® M700, as well as corn syrup solids such as MALTRIN® M200 and MALTRIN® M250 (these having a DE>25). The invention limited to malto-oligosaccharides species, and is not indeed, any suitable polysaccharide may be employed as a starting material in conjunction with the present invention.

In accordance with the invention, the starting material comprising the polysaccharide or mixture polysaccharides is substantially reduced, in some cases to a DE of essentially zero, under conditions suitable to substantially preserve the DP profile of the starting By "substantially reduced" is meant that the materials. DE of the reduced polyosaccharide is reduced by at least about 85%, and preferably at least about 90%, relative to the initial DE of the polysaccharide starting materials. The term "essentially zero" as used herein with respect to DE value refers to a hydrogenated product having a DE of less than about 1. By "substantially preserved" used herein with respect to DP profile is meant that, the reduced product, the oligosaccharide percentage of at least a majority of the polysaccharide species having a given DP value does not differ by more than about 7%, preferably no more than about 4%, more preferably no more than about 2%, and most preferably no more than about 0.75%, based on 100% of the polysaccharide species and

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relative to the corresponding species of like DP value in the starting material prior to reduction.

The hydrogenation of the polysaccharide accomplished in any suitable manner. For example, in one embodiment of invention, the hydrogenation the is accomplished chemically, using sodium borohydride or donor. Preferably, another hydride however, the accomplished catalytically, hydrogenation is in the presence of a metal catalyst suitable for catalyzing the hydrogenation of the polysaccharide in the presence of Examples of suitable hydrogenation catalysts hydrogen. include palladium, platinum, ruthenium, rhodium, nickel. The metal catalyst may be in the form of the neutral metal, or may be in the form of suitable metal alloy, oxide, salt, or organometallic species. Preferably, the catalyst is nickel or an activated nickel species, (such as a molybdenum promoted nickel species). Examples of suitable commercially available catalysts include A-7063 (Activated Metals and Chemicals, Inc.); H-(Engelhard); Raney<sup>TM</sup> 3110, 3111, and 3201 (Davison Chemical); and BK113W (Degussa), with the most preferred catalyst being Raney<sup>TM</sup> 3110. The catalyst may be employed in any amount effective to catalyze hydrogenation of the polysaccharide species, and preferably is present in an ranging from about 0.5 to about ∙10% (w/w)polysaccharide) in the reaction mixture.

The hydrogenation of the malto-oligosaccharide or other polysaccharide is accomplished under pressures and temperatures suitable to maintain the DP profile thereof. In some embodiments, the reaction pressure preferably

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ranges up to about 1500 psi. More preferably, pressure ranges from about 200 psi to about 1200 psi; even more preferably the pressure ranges from about 400 psi to about 700 psi. In other embodiments of the invention, the pressure ranges up to about 3000 psi. 5 instance, the pressure can range from about 1500 to about 3000 psi; from about 1500 to about 2500 psi; or from about 2000 The about 1500 psi to psi. reaction temperature preferably ranges from about 50 to about 150° C; more preferably, the temperature ranges from about 10 to about 130° C; even more preferably, С temperature ranges from about 110° C to about 120° When pressures above about 1500 psi are employed, reaction temperature most preferably is about 15 Hydrogen optionally may be introduced into the reaction vessel at any rate effective to reduce polysaccharide. Preferably, the vessel is filled with hydrogen, and additional hydrogen is added a purge rate of up to about 2.5 L/min for a 2.0L reaction vessel.

The reaction may take place in any medium suitable to effectuate the hydrogenation of the saccharide mixture. Preferably, the reaction takes place in an under pH conditions suitable for aqueous medium, hydrogenation reaction to proceed. The pH of the medium preferably ranges from about 3.5 to about 8.5, preferably from about 4.5 to about 6.5, and even more preferably from about 5 to about 6. The invention is generally contemplated in some embodiments to comprise catalytically reducing a polysaccharide step of mixture in aqueous solution at the specified pH ranges.

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For example, the invention encompasses a method comprising the steps of providing an oligosaccharide or oligosaccharide mixture, such as a malto-oligosaccharide mixture, and catalytically hydrogenating the mixture in aqueous solution at a pH ranging from about 3.5 to about 8.5.

To ensure adequate hydrogenation under these temperatures and pressures, the reaction mixture should be vigorously agitated. Hydrogenation should proceed for a time sufficient for the DE value of the polysaccharide mixture to be reduced to essentially zero. In preferred embodiments of the invention, the reaction time ranges from about 0.5 hours to about 72 hours, more preferably, from about 1 hour to about 8 hours, even more preferably, about 2 to about 4 hours.

The reaction may be performed in a catalytic bed containing the metal catalyst. In accordance with this embodiment of the invention, the polysaccharide and hydrogen are continuously introduced into the reaction bed under conditions sufficient to reduce the DE of the polysaccharide to a value of essentially zero while maintaining the DP profile. The temperature and pressure conditions in the catalytic bed may be substantially as hereinbefore described.

Surprisingly, it has been found that reduced maltooligosaccharides prepared in accordance with the present invention have low light absorbance values. For example, in preferred embodiments of the invention, the absorbance of the reduced malto-oligosaccharide is less than about 0.25; more preferably, the absorbance is less than about

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0.15, after holding a solution of the maltooligosaccharide at 75° C and pH 10 for two hours. As used herein, the absorbance refers to the absorbance at 450 nm the malto-oligosaccharide, 10% solution of of measured in a 1 cm cell. In contrast, the UV absorbance of MALTRIN® M100, a product which has a DE of about 10, about 0.73 after being treated under the is conditions. The surprisingly low light absorbance of the reduced malto-oligosaccharides of the present invention aforementioned reaction stressing under the after 10 conditions indicates an enhanced resistance to color formation.

malto-oligosaccharides and other The reduced polysaccharides prepared in accordance with the process of the invention may be used in most or all applications in which a non-reduced polysaccharide was previously With respect to at least malto-oligosaccharides, used. include film-forming applications of such examples agents; bulking agents, carrying agents for dry products or capsules; fillers for products such as creams and roller compaction/granulation binders for applications; medical and nutritional agents; soaps and spray-drying agents; tableting cleansers; sweetness controllers; crystallization inhibitors; reduced maltocryoprotectants; and so forth. The oligosaccharides of the invention are believed to be substantially unreactive toward proteinaceous species, thus potentially leading to enhanced properties related applications. Of course, the invention is not foregoing specific limited in applicability to the

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applications, and the process and product of the invention may find utility in other applications as well.

For example, the reduced malto-oligosaccharides may be used in a method for freezing a biological sample, the biological sample being a cell, tissue, protein, DNA, or other sample. It is known in the art to lyophilize such samples by forming an aqueous solution of the sample, and then to remove water from the solution. Maltodextrins are commonly used as cryoprotectants to protect the sample against damage caused by ice crystallization during lyophilization. One problem with the use of conventional maltodextrins as cryoprotectants is that the reactivity of malto-oligosaccharides causes unwanted reactions. such as glycosylation or cross-linking The reduced malto-oligosaccharides of proteins. present invention may be employed in a method that includes the steps of providing a biological sample in an aqueous solution, adding to the sample a reduced maltooligosaccharide to form a combination, and lyophilizing combination. The reduced malto-oligosaccharide of preferably is а mixture malto-oligosaccharides prepared in accordance with the foregoing teachings. has surprisingly been found that the reduced maltooligosaccharides prepared in accordance with the invention function well as cryoprotectants, the and reduced reactivity protects against reaction with proteins and other nitrogen-containing species.

The following examples illustrate preferred embodiments of the invention, but should not be construed as limiting in scope.

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# Example 1 Reduction of Maltodextrin

In 650 ml of deionized water was dissolved 567 g of MALTRIN® M100 maltodextrin (5.6% moisture). Sodium borohydride, 28.5 ml (12% solution, 14M NaOH) was slowly added to the stirred mixture at ambient temperature. The initial pH of the solution was measured and found to be pH 11.8.

The mixture was stirred overnight (17.5 hrs.) and quenched by adjusting the pH with 7% HCl solution to a pH of 7.3. The sample was then frozen and freeze-dried to yield 573 g of product, the product including 2% moisture and 5.37% ash.

A 393 g sample of product was prepared by purifying the product by passing the product through two series of alternating columns of DOWEX<sup>TM</sup> MONO 88 strong cationic exchange resin in the hydrogen form, and of DOWEX<sup>TM</sup> MONO 66 weak anionic exchange resin in the free base form. The DP profile was then determined.

The following results were obtained:

	Approximate DP	DP profile of
DP	profile of	Reduced Maltodextin
	MALTRIN® M100	Mixture
	(as measured via	(% dry solid basis)
	HPLC analysis)	·
	(% dry solid basis)	
DP>8	67.3%	67.0%
	_	
DP 8	4.6%	4.6%
77.5	6.00	7 10
DP 7	6.9%	7.1%
DP 6	5.9%	6.0%
DP 5	3.1%	3.4%
DP 4	3.8%	3.8%
DP 3	4.4%	4.5%
DD 2	2 0%	2 7%
DP 2	2.8%	2.7%
DP 1	1.0%	0.2%

The DE value of the MALTRIN® M100 starting material was 11.8. In contrast, the DE value of the reduced maltodextrin mixture was 0.8.

Thus, it is seen that the DE of the maltodextrin mixture was reduced to a DE of essentially zero, while the DP profile was substantially preserved.

# 10 Example 2 Catalytic Maltodextrin Reduction

To 450 ml water was added 265 g MALTRIN $^{\odot}$  M100 maltodextrin (5.5% moisture). The mixture was stirred

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for 30 minutes at room temperature to obtain a clear solution. To the solution was added 22.4g of a 50% slurry of activated nickel (Acros) in water (9% w/w catalyst/maltodextrin). This solution was stirred for another 10 minutes, and the pH was measured as pH 8.5.

The mixture was transferred to a 2.0L Parr 4522M reactor. The reactor was sealed and stirring was commenced at 550 rpm. Subsequently, the reactor was pressurized to 1150 psi with hydrogen gas and heated to 115° C to initiate hydrogenation of the maltodextrin. After five hours, the reaction was stopped by cooling, and the vessel was then depressurized.

The reaction contents were filtered through Whatman No. 1 filter paper to give a clear viscous solution having a pH of 6.85 and 33% solids. About 250 g of material having an ash content of about 0.16% was recovered. The sample was combined with products from replicate hydrogenation runs, ion exchanged as in Example 1, and freeze dried.

This experiment was repeated ten times with selected pressure, temperature, and stirring ranges, and the following results were obtained.

 1300	130	009	TRIAL	10	65.9	4.6	7.2	6 4.	3.3
1000	130	400	TRIAL	o,	65.5	4.7	7.4	6.5	3.5
1300	100	400	TRIAL	ω	66.4	4.6	7.3	4.	3.3
1300	100	009	TRIAL	7	66.7	4.6	7.4	6 4.	3.3
1300	130	400	TRIAL	9	64.6	4.7	7.3	6.5	3.5
1000	130	009	TRIAL	ഗ	0.99	4.6	7.4	6	3.4
1000	100	400	TRIAL	4	9.99	4.6	7.4	6.4	3.4
1000	130	009	TRIAL	м	65.6	4.7	7.4	ه. ت	3.4
1150	115	200	TRIAL	7	66.1	4.7	7.4	6 4.	3.4
1000	100	009	TRIAL	ч	65.0	4.4	7.2	6.3	4.2
psi	Temp (° C)	Rpm	CONTROL		67.3	9.4	6. 9	5. 9.	3.1
			DP PROFILE		DP>8	DP 8	DP 7	DP 6	DP 5

. 8	4.4	2.8	1.5	0.4
3.9	4.5	8 .	1.5	<0.5
		2.7	8.0	0.6 0.8
3.8 3.8	4.4 4.5	2.7	8.0	9.0
3.9	4.5	2.8	2.2	0.3
8	4.5	2.8	1.0	<0.5
3.8	4.4	2.7	8.0	0.98
3.8	4.5	2.8	1.4	<0.5
3.8	4.5	2.8	1.0	<0.5
4.1	4.2	2.7	8.0	9.0
3.8	4.4	2.8	1.0	11.8
DP 4	DP 3	DP 2	DP 1	DE

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The best results in this reactor were obtained when hydrogenation pressure was between 1000 and 1300 psi, temperature was between 100°-130° C, and impeller speed was >500 rpm. It is further contemplated that as the hydrogen purge rate and agitation are increased, lower reaction temperatures and pressures are realizable thereby. In other reactors, higher pressures may be optimal.

As demonstrated, the DP profile of the starting naterial was substantially preserved upon reduction in each case, while the DE was reduced to a value of essentially zero.

# Example 3 Catalytic Maltodextrin Reduction

MALTRIN® M180 maltodextrin, 519 g (5.5% moisture) was added to 881 ml water and stirred for approximately 30 minutes to obtain a clear solution. Raney<sup>tm</sup> nickel GD3110 (Grace Davison), 18.4 q · (3.7% dry solids basis catalyst/maltodextrin w/w) was added and the mixture was stirred for another 10 minutes at room temperature. entire mixture (ca. 35% solids) was then transferred to a The unit was sealed and 2.0L Parr 4522 M reactor. stirring was continued at 600 rpm. The Parr reactor was pressurized to 500 psi with hydrogen gas and heated to 120° C. After 4 hours at 120° C, the reaction was stopped cooling and then depressurization. The reaction contents were filtered through Whatman No. 1 filter paper to give a clear viscous solution. The sample was then ion exchanged as set forth in Example 1. No detectable ash was found after ion exchange. The sample was freeze dried after ion exchange to yield a maltodextrin mixture having a DE of 0.46, an ash content of 0%, and the following DP profile.

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DP profile (% dry solids
basis)
46.2%
4.0%
4.0%
9.4%
11.1%
5.9%
6.4%
8.5%
6.4%
2.0%
0.46

# Example 4 Absorbance Evaluation

Samples of MALTRIN® M100 maltodextrin, ion-exchanged MALTRIN® M100 maltodextrin, and reduced MALTRIN® M100 maltodextrin (from Example 1) were held at 75° C for two hours in solution at a pH of about 10. The absorbance of a 10% solution of each sample was thereby obtained using a 1 cm cell.

C	Δ	м	D	T.	F
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# ABSORBANCE (10%/1cm)

MALTRIN® M100

0.74

Reduced MALTRIN® M100

0.07

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As shown, the 450nm absorbance of reduced MALTRIN® M100 maltodextrin is significantly lower as compared to non-reduced MALTRIN® maltodextrins, thus indicating a lower reactivity. It is believed that the decrease in absorbance is largely due to the reduction of the maltodextrin in accordance with the invention.

# Example 5 Catalyst Evaluation

This example comparatively evaluates a number of activated nickel catalysts.

To 900 ml water was added 600 g MALTRIN® M180 maltodextrin (5% moisture). The mixture was stirred for 30 minutes at room temperature to ensure dissolution, then poured into a 2.0L Parr 4522M reactor. Activated sponge nickel was added to the reactor (3.7% w/w catalyst/maltodextrin), after which the reactor was sealed and stirred at 600 rpm.

The reactor was pressurized to 1000 psi and heated to 110° C. Hydrogen was introduced into the reaction at a rate of about 0.5 L/min. A sample of the reaction mixture was taken after 2 hours, and the reaction was stopped after four hours and a final sample taken. The experiment was repeated several times.

The samples were filtered, ion-exchanged, and freezedried as before, and then evaluated for DE and DP profile. DE was evaluated over a number of runs for each sample.

Average DE

Catalyst	Avg. DE (2 hr)	Avg. DE (4 hr)
AM&C		
A-7063	1.93	0.86
Raney™ GD 3110	1.75	0.77
Raney™ GD 3111	3.44	1.14
Raney™ GD 3201	6.17	3.32
Engelhard H-102	2.13	0.82
Degussa BK 113W	2.93	0.91
Acros (generic)		2.08
		(5.4 hrs)

As shown in the foregoing table, most of the listed catalysts were satisfactory. It was found that pressure could be decreased to as low as about 600 psi with a concomitant temperature to about 130° C and an increase in purge rate to about 2 L/min.

The DP profile was evaluated after four hours reaction time under various conditions (impeller speed was 600 rpm in each case). The following results were observed for several of the runs.

# DP Profile (% dry solids basis)

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		Raney GD3110	Engelhard H-107	AM&C A-7063	Raney GD3110	Degussa BK 113W	Degussa BK 113W	Raney GD3110
Pressure (psi)		1000	1000	1000	750	1000	1000	009
Temp (°C)		110	110	110	130	110	110	130
	MALTRIN <sup>®</sup> M180 control	1	73	33	4.	ري د	9	7
	44.8	44.6	45.3	44.0	44.0	44.40	44.3	44.4
	3.9	3.9	3.9	4.0	4.0	4.0	3.8	3.9
	10.0	10.0	10.0	10.0	9.8	9.9	9.8	6.6
	12.0	11.9	12.0	11.9	11.7	11.8	11.7	11.8
	5.8	6.1	5.9	6.1	6.2	6.1	6.1	6.2
	6.5	9.9	6.4	9.9	9.9	9.9	9.9	9.9

Catalyst		Raney GD3110	Engelhard H-107	AM&C A-7063	Raney GD3110	Degussa BK 113W	Degussa BK 113W	Raney GD3110
DP 3	8.5	8.7	8.5	8.8	8.8	8.9	8.9	8.8
DP 2	6.5	6.4	6.3	8.9	6.7	6.7	6.7	
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DP 1	1.9	1.7	1.7	1.6	1.8	1.7	1.8	1.8
DE % solids	~18	1.23	1.46	0.219	0.087	0.409	1.315	0.095

As shown, the DP profile of the starting maltooligosaccharide mixture was substantially preserved, while the DE was reduced to essentially zero or was substantially reduced in each case.

# Example 6

MALTRIN® M040 maltodextrin was catalytically hydrogenated in the same manner as in Example 3. Samples of reduced malto-oligosaccharide were obtained thereby in two separate runs. The DP profile and DE value for each run was evaluated, and the following results were obtained:

DP Profile (% dry solids basis)

	MALTRIN® M040 Control	Run 1	Run 2
DP>8	92.9	91.7	89.8
DP 8	0.7	0.7	0.9
DP 7	1.1	1.2	1.7
DP 6	1.1	1.3	1.7
DP 5	0.8	1.0	1.2
DP 4	1.1	1.2	1.4
DP 3	1.2	1.4	1.6
DP 2	0.7	0.8	1.1
DP 1	0.3	0.4	0.4
DE	~5	0.502	0.62

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These results illustrate that, for each run, the DP profile was substantially preserved, while the DE value was reduced to a value of substantially zero.

# Example 7 Temperature Stability

This example illustrates the improved temperature stability of the reduced malto-oligosaccharide of the invention.

MALTRIN® M180, M100 M040 Samples of and comparatively evaluated against hydrogenated samples of M180, M100, and M040 using a TLA 2050 Thermogravimetric Analyzer (TA Instruments Inc., New Castle, DE). To the analyzer pan was added 5.000-8.000 mg of the sample (in separate test runs). Each sample was heated from 25° C to 600° C at 10° C/min in oxygen (purge rate of 100 cm³/min). The onset of weight change of the sample was taken as the onset of thermal degradation. The following results were obtained.

Sample	Onset of Degradation Temperature (°C)	Temperature Stability Increase
	_	(Δ°C)
M180	263.2	
Hydrogenated M180	286.2	23.0
M100	270.4	
Hydrogenated M100	292.2	21.8
M040	270.2	
Hydrogenated M040	288.1	17.9

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These results demonstrate that the reduced maltooligosaccharides of the invention have an improved thermal stability as compared with their non-reduced counterparts.

Example 8

Example 3 is repeated, except that the hydrogenation is performed in a pressure vessel at a pressure of 2500 psi.

While particular embodiments of the invention have been shown, it will be understood that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings. It is, therefore, contemplated by the appended claims to cover any such modifications as incorporate those features which constitute the essential features of these improvements within the true spirit and scope of the invention. All references cited herein are hereby incorporated by reference in their entireties.